

Extraction of lanthanides from nitric acid solution using *isobutyl*-BTP/ionic liquid system\*

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Extraction behavior of lanthanides (La, Eu, Dy, Lu) from HNO<sub>3</sub> solution was studied using a novel extraction system with hydrophobic ionic liquid being diluent and *isobutyl*-BTP being extractant. Compared with that in *isobutyl*-BTP/cyclohexane extraction system, application of ionic liquid as the extracting phase provided unprecedented enhancement of the extraction performance of *isobutyl*-BTP for lanthanides. It was found that the *isobutyl*-BTP/[C<sub>n</sub>mim][NTf<sub>2</sub>] extraction system is favorable to get good extraction at low acidity condition (< 0.1 M). Of all the *isobutyl*-BTP/[C<sub>n</sub>mim][NTf<sub>2</sub>] (*n* = 2, 6, 8) systems, *isobutyl*-BTP/[C<sub>2</sub>mim][NTf<sub>2</sub>] extraction system provides the best extraction performance and fastest extraction kinetics within 5 min towards Dy<sup>3+</sup>. The extraction is spontaneous endothermic and temperature is good for extraction. The transfer of lanthanides, in *isobutyl*-BTP/[C<sub>2</sub>mim][NTf<sub>2</sub>] extraction system, proceeded via a cation exchange mechanism, in contrast to extraction of neutral complex in the cyclohexane system.

Keywords: Lanthanides, Extraction, Ionic liquids, *isobutyl*-BTP

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## I. INTRODUCTION

Lanthanides (Ln) recycling from industrial residues has become economically interesting with the widely application of Ln compounds [1–3]. In addition, the Ln and actinides (An) should be co-extracted from nuclear waste for the subsequent An/Ln separation [4, 5]. For these reasons, various organic compounds have been investigated to obtain an appropriate extractant for Ln. Musikas *et al.* [6, 7] extracted Ln with some diamides dissolved in alkanes and found that 3-oxapentanediamides showed high extractability for some Ln. Drew *et al.* [8] studied the complexation of various aza-aromatic based on the Ln series (La-sm). However, an effective extraction in conventional organic diluent needs to be accomplished under high acidic conditions, as the predominant mode of cation transfer from aqueous phase into organic phase has been proved as neutral complex mechanism. For example, Narita *et al.* [9] noted that chloroform solution containing N,N'-dimethyl-N,N'-diphenyl-3-oxapentanediamide showed the distribution ratio of Lu about 100 from 3 M HNO<sub>3</sub>. Therefore, the subsequent acid degradation of extractants under high acidity will severely restrict their industrial application.

Ionic liquids (ILs) have been identified as ideal alternative solvents in liquid-liquid extraction due to their unique properties such as negligible vapor pressure, good thermal, chemical stability and good dissolving ability, etc. [10–13]. Also, it has been noted that Ln cations can be extracted from aqueous

phase into the ILs phase through cation exchange mechanism without adding acids [14–16]. Dietz *et al.* [14] reported that 1-*amyl*-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imides ([C<sub>5</sub>mim][PF<sub>6</sub>]) solution containing dicyclohexano-18-crown-6 showed a high distribution coefficient of strontium at low acidity as the cation exchange between [C<sub>5</sub>mim]<sup>+</sup> and Sr<sup>2+</sup>. Nakashima *et al.* [15] reported that 1-*butyl*-3-methyl-imidazolium hexafluorophosphate [C<sub>4</sub>mim][PF<sub>6</sub>] solution containing 3 mM octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide could extract 90% of Ce<sub>3</sub><sup>+</sup> from deionized water, since the [PF<sub>6</sub>]<sup>−</sup> anion plays a key role in the electrically neutralization of the Ln<sup>3+</sup> · 3 CMPO complex. Therefore, the application of ILs would construct the low acidity extraction system to enhance the stability of extraction system.

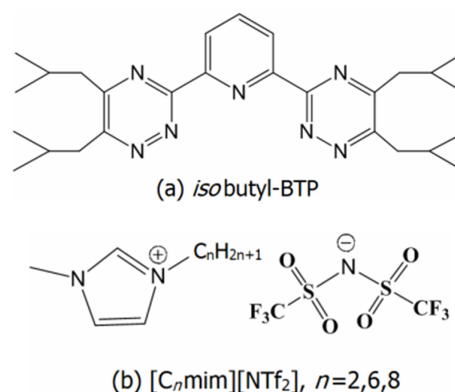


Fig. 1. Chemical structures of *isobutyl*-BTP and [C<sub>n</sub>mim][NTf<sub>2</sub>].

In present study, an extraction system consisted of 2,6-bis(5,6-dihexyl-1,2,4-triazin-3-yl) pyridine (*isobutyl*-BTP) as extractant (Fig. 1(a)) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>n</sub>mim][NTf<sub>2</sub>]) as diluents (Fig. 1(b)) was designed. The extraction behavior of sev-

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eral Ln ions (La, Eu, Dy, Lu) from low acidity  $\text{HNO}_3$  solution was studied. The *isobutyl*-BTP/cyclohexane system was investigated for comparison purpose.

## II. EXPERIMENTAL

### A. Materials

The *isobutyl*-BTP (> 95%) was synthesized according to Ref. [17].  $[\text{C}_n\text{mim}][\text{NTf}_2]$  (purity > 99%) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). No impurities were detected using  $^1\text{H}$  NMR spectrometry. The other organic and inorganic compounds were commercial products of reagent grade and used without further purification. Stock solutions of  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Lu}^{3+}$  were prepared by dissolving their nitrate into  $\text{HNO}_3$  solution.

### B. Method

#### 1. Solvent extraction

The extraction phase (2.0 mL) containing 25 mM *isobutyl*-BTP was prepared by dissolving *isobutyl*-BTP in  $[\text{C}_n\text{mim}][\text{NTf}_2]$ , and the aqueous solution (2.0 mL) containing  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Lu}^{3+}$  (2 mM for each species) was prepared in  $\text{HNO}_3$  medium in concentration of 0.01, 0.1, 0.5, 1, 2 and 3 M. The extraction experiments were conducted by contacting the extraction phase with aqueous solution for designated time in a constant temperature incubator shaker which maintained a thermo-stated water bath at  $25^\circ\text{C}$  with a rotating speed of 120 rpm, followed by centrifuging for 3 min to ensure that two phases were completely separated. After phase separation, the aqueous solution was diluted with deionized water, and Ln concentration in the diluted aqueous solution was measured by Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICPS-7510, SHIMADZU, JPN). The extraction experiment against Ln using *isobutyl*-BTP/cyclohexane extraction system was carried out in the same condition.

The distribution ratios ( $D$ ) and extraction efficiencies ( $E$ ) were calculated with Eqs. (1) and (2), respectively, where  $M$  means the cation species in aqueous phase, the subscript org/aq is short for organic phase/aqueous phase, while the subscript "i/f" designates the initial/final concentration of metal ions in the diluted solution.

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} = \frac{[M]_{\text{aq,i}} - [M]_{\text{aq,f}}}{[M]_{\text{aq,f}}}, \quad (1)$$

$$E\% = \frac{[M]_{\text{aq,i}} - [M]_{\text{aq,f}}}{[M]_{\text{aq,i}}} \times 100. \quad (2)$$

#### 2. UV-visible analysis of cation in the IL

The content of  $[\text{C}_2\text{mim}]^+$  in aqueous phase after extraction was quantified using UV-Visible spectrophotometry (SHIMADZU UV-3600 PC spectrophotometer). Calibrations were performed using the standards with a series of initial concentration of the  $[\text{C}_2\text{mim}]\text{Cl}$  dissolved in water. The characteristic band was selected at 210 nm due to its relative high signal intensity.

#### 3. Back extraction experiment of *isobutyl*-BTP/ $[\text{C}_2\text{mim}][\text{NTf}_2]$ against $\text{Dy}^{3+}$

Extraction experiments have been described above. After extraction of  $\text{Dy}^{3+}$  at 0.01 M  $\text{HNO}_3$ , it was centrifuged to separate out aqueous phase and IL phase and then took the IL phase (1 mL) into back extraction agent (1 mL)  $\text{H}_2\text{O}$ , 1 M  $\text{HNO}_3$ , 3 M  $\text{HNO}_3$ , 0.01 M DTPA (Diethylene triamine pentacetate acid) and 0.5 M Thiourea to oscillate under the same condition for 48 h. The concentration of  $\text{Dy}^{3+}$  was analyzed by ICPS-7510 (SHIMADZU, Japan).

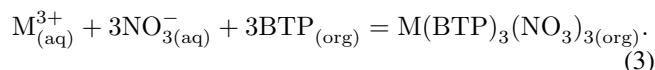
## III. RESULTS AND DISCUSSION

Firstly, we investigated the extraction of Ln using ILs alone in the absence of *isobutyl*-BTP, to find that the ILs alone can hardly extract Ln. This is similar to the work reported by Shimojo *et al.* [18]. But in a solubility experiment, we found that  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ( $n = 2, 6, 8$ ) was of excellent solubility against *isobutyl*-BTP.

### A. Extraction of $\text{Dy}^{3+}$ in different extraction systems

The distribution ratio of  $\text{Dy}^{3+}$  ion ( $D_{\text{Dy}}$ ) as function of  $\text{HNO}_3$  concentration for the *isobutyl*-BTP/ $[\text{C}_n\text{mim}][\text{NTf}_2]$  systems and the *isobutyl*-BTP/cyclohexane system are shown in Fig. 2.

In the cyclohexane system, the  $D_{\text{Dy}}$  increased with  $\text{HNO}_3$  concentration, indicating that the anion  $\text{NO}_3^-$  enhances extractability due to neutral complex structure. The extraction mechanism can be expressed as Eq. (3) [19]:



In the *isobutyl*-BTP/ $[\text{C}_n\text{mim}][\text{NTf}_2]$  systems,  $D_{\text{Dy}}$  decreased rapidly with increasing  $\text{HNO}_3$  concentration from 0.01 M to 1 M, where it began to increase slightly. The curves differ from each other because of the mechanism transition depending on acidity variation.  $\text{H}^+$  is a competitive species in cation exchange, hence the higher  $D_{\text{Dy}}$  with the lower concentration of  $\text{H}^+$ ; but when the  $\text{H}^+$  concentration is great enough to restrain the cation exchange, the neutral extraction becomes the dominant extraction mechanism. As a consequence, the  $D_{\text{Dy}}$  increases slightly with the acidity, just like in the cyclohexane system.

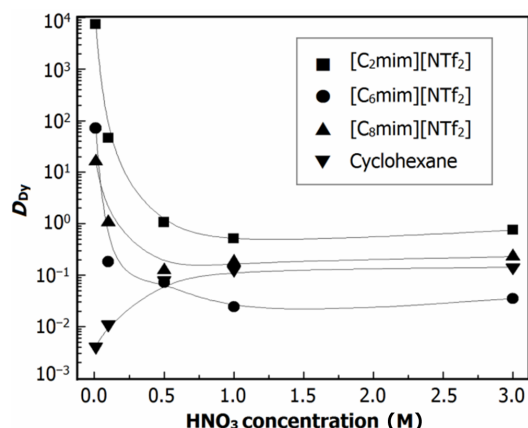


Fig. 2. Distribution ratio for extracted  $Dy^{3+}$  ion by IL phase or by cyclohexane, as function of the  $HNO_3$  concentration.

Based on the above discussion, the  $HNO_3$  concentration of 0.01 M was used in the following experiments using *isobutyl*-BTP/ $[C_nmim][NTf_2]$  system.

#### B. Extraction kinetics of *isobutyl*-BTP/ $[C_nmim][NTf_2]$ extraction system

The extraction kinetics reflects basic properties of the extraction system, so the *isobutyl*-BTP/ $[C_nmim][NTf_2]$  extraction experiments in different contacting time were carried out. In the *isobutyl*-BTP/ $[C_2mim][NTf_2]$  system, significant advantage in extraction kinetics was observed (Fig. 3). Its extraction kinetics of  $Dy^{3+}$  reached equilibrium in 5 min, about 1000 times faster than that in the *isobutyl*-BTP/ $[C_nmim][NTf_2]$  ( $n = 6, 8$ ) system, which spent dozens of hours to reach equilibrium. This indicates that both hydrophobicity and viscosity of imidazolium are impeditive to the cation exchange [21]. Longer alkyl chain of IL would improve the hydrophobicity and viscosity. Therefore,  $[C_2mim][NTf_2]$  was chosen as the diluent for the following Ln extraction.

#### C. Determination of thermodynamic parameters

Temperature effect on the extraction of Dy from 0.01 M  $HNO_3$  using 20 mM *isobutyl*-BTP/ $[C_2mim][NTf_2]$  system was studied. As shown in Fig. 4,  $D_{Dy}$  increased with temperature, indicating an endothermic process of the extraction. The change in enthalpy ( $\Delta H$ ) during the extraction can be calculated by the Van't Hoff equation

$$\Delta H = -2.303R \Delta \lg D / \Delta(1/T). \quad (4)$$

A plot of  $\lg D$  vs.  $1/T$  gives a straight line with a slope of  $-\Delta H/2.303R$ , while the change in Gibbs's free energy ( $\Delta G$ ) can be calculated by

$$\Delta G = -2.303RT \lg K. \quad (5)$$

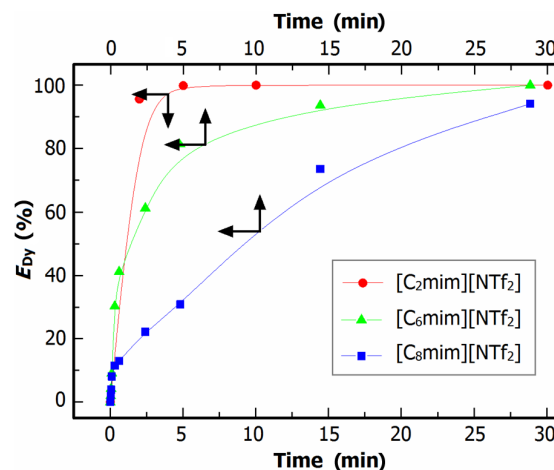


Fig. 3. (Color online)  $Dy^{3+}$  extraction kinetics by *isobutyl*-BTP/ $[C_nmim][NTf_2]$  in 0.01 M  $HNO_3$ .

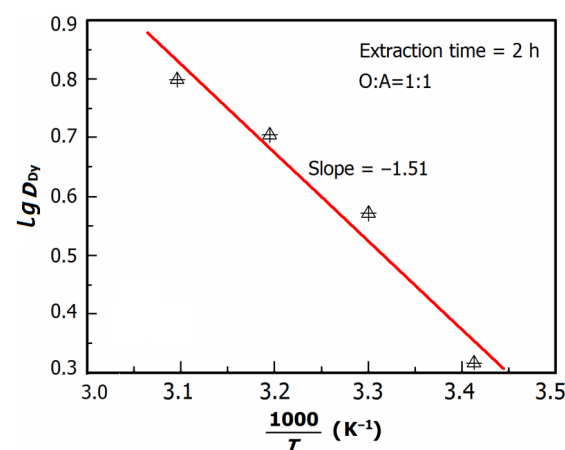


Fig. 4. (Color online) Distribution ratio of Dy vs. temperature in  $[C_2mim][NTf_2]$  with 0.01 M  $HNO_3$  and 20 mM *isobutyl*-BTP.

The change in entropy ( $\Delta S$ ) at a particular temperature can be calculated by

$$\Delta s = (\Delta H - \Delta G)/T. \quad (6)$$

From Eqs. (4), (5) and (6), the values of  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  are 28.91, 19.86 and 30.37 kJ/mol, respectively. Therefore, the extraction is spontaneous endothermic. Temperature increase is good for extraction.

#### D. Extraction mechanism of Ln using *isobutyl*-BTP/ $[C_2mim][NTf_2]$ system

In order to check the proposed cation exchange mechanism, we carried out extraction experiments in deionized water by mixing the aqueous solutions of  $EuCl_3$  with  $[C_2mim][NTf_2]$ . Since  $DyCl_3$  has a poor water solubility, and ultraviolet absorption of  $NO_3^-$  has strong interference on  $[C_2mim]^+$  cation, herein we chose  $EuCl_3$ . As shown in

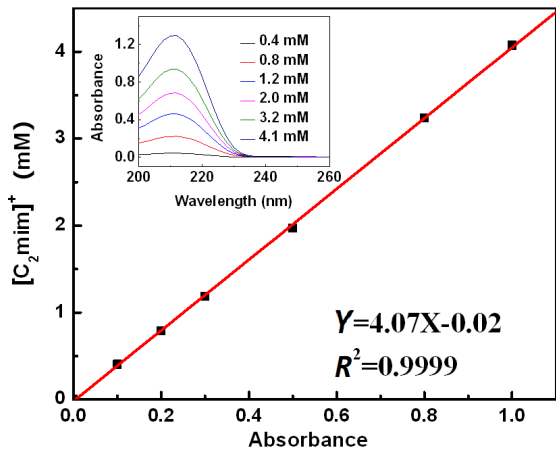
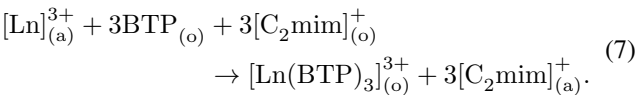


Fig. 5. (Color online) Calibration curves of  $[\text{C}_2\text{mim}]^+$  tested by UV-visible analysis.

Fig. 5, calibration curves of  $[\text{C}_2\text{mim}]^+$  was used to measure the concentration of  $[\text{C}_2\text{mim}]^+$  in the aqueous phase transferred from  $[\text{C}_2\text{mim}][\text{NTf}_2]$ . We measured the  $\text{Eu}^{3+}$  concentration in  $[\text{C}_2\text{mim}][\text{NTf}_2]$  transferred from the aqueous phase, and  $[\text{C}_2\text{mim}]^+$  in the aqueous phase transferred from  $[\text{C}_2\text{mim}][\text{NTf}_2]$ . The results were plotted against each other in Fig. 6, being linear with a slope of 2.84. Due to experiment error, we considered the slope of 3. This indicates that a cation exchange mechanism is occurring with three cations from the IL involved. Therefore, the extraction equilibrium equation at low  $\text{HNO}_3$  concentration can be suggested as



In the equation, the stoichiometric ratio of  $\text{Dy}^{3+}$  to BTP is based on previous investigation [20].

#### E. Extraction of Ln in *isobutyl*-BTP/ $[\text{C}_2\text{mim}][\text{NTf}_2]$ system

To assess the extraction performance of *isobutyl*-BTP/ $[\text{C}_2\text{mim}][\text{NTf}_2]$  extraction system for Ln, ion species of  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Lu}^{3+}$  were employed as light, middle, middle, and heavy Ln, respectively. As shown in Table 1, the order of extraction efficiency for Ln was  $\text{Eu}^{3+} > \text{Dy}^{3+} > \text{Lu}^{3+} > \text{La}^{3+}$ , indicating that *isobutyl*-BTP/ $[\text{C}_2\text{mim}][\text{NTf}_2]$  system is inclined to extract  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$ . Therefore, we suppose that the ionic size of dysprosium and europium are particularly suitable for coordination.

#### F. Back extraction

The stripping of  $\text{Dy}^{3+}$  from the  $[\text{C}_2\text{mim}][\text{NTf}_2]$  was carried out for further knowledge of recycling. Several complexing agents were chosen, including 0.01 M DTPA, 0.5 M Thiourea and high concentration of  $\text{HNO}_3$ . Pure water was

TABLE 1. Extraction efficiency of several Ln using *isobutyl*-BTP/ $[\text{C}_2\text{mim}][\text{NTf}_2]$  system at 0.01 M  $\text{HNO}_3$

Ln	Ionic radius (Å)	Extraction efficiency (%)
La	1.061	80.79
Eu	0.950	99.78
Dy	0.908	99.08
Lu	0.848	94.92

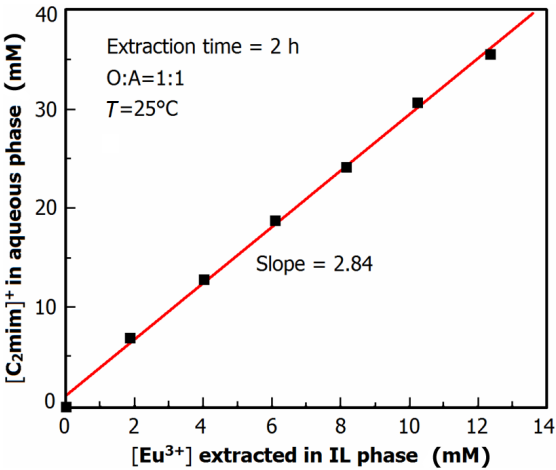


Fig. 6. (Color online) A plot of  $[\text{C}_2\text{mim}]^+$  against  $\text{Eu}^{3+}$  for extraction of  $\text{Eu}^{3+}$  from the aqueous phase to the IL phase in deionized water.

chosen as comparison. As shown in Table 2, the  $\text{Dy}^{3+}$  was stripped completely at 3 M  $\text{HNO}_3$ , and other back extraction agent did not function. Considering the extraction behavior referred above, we think that Dy and *isobutyl*-BTP complexation ( $[\text{Dy}(\text{BTP})_3]^{3+}$ ) in the IL phase is instability at high acidity, hence the strip of Dy ion at 3 M  $\text{HNO}_3$ . Maybe, this cannot be called back extraction. Further efforts will be made to find good back extraction agent of Dy without resulting in instability of  $[\text{Dy}(\text{BTP})_3]^{3+}$ .

TABLE 2. Stripping efficiency of  $\text{Dy}^{3+}$  from *isobutyl*-BTP/ $[\text{C}_2\text{mim}][\text{NTf}_2]$  system using various stripping solution

Stripping solution	Stripping efficiency (%)
$\text{H}_2\text{O}$	0.43
1 M $\text{HNO}_3$	0.69
3 M $\text{HNO}_3$	100
0.01 M DTPA	0.35
0.5 M Thiourea	0.39

#### IV. CONCLUSION

A novel extraction system based on *isobutyl*-BTP/ $[\text{C}_n\text{mim}][\text{NTf}_2]$  was developed for Ln extraction. The system provided high extraction performance for Ln compared with cyclohexane. Of all the *isobutyl*-BTP/ $[\text{C}_n\text{mim}][\text{NTf}_2]$  systems ( $n = 2, 6, 8$ ), *isobutyl*-BTP/ $[\text{C}_2\text{mim}][\text{NTf}_2]$  system provides the best extraction

performance and the fastest extraction kinetics within 5 min towards  $\text{Dy}^{3+}$ . It was found that the *isobutyl*-BTP/[C<sub>2</sub>mim][NTf<sub>2</sub>] system is inclined to extract at low acidity conditions, and can be stripped at high  $\text{HNO}_3$ . The extraction mechanism based on the cation exchange was reasonably proposed for the novel extraction system. In addition,  $\text{Dy}^{3+}$  was found to be favor extracted in current

extraction system. The extraction is spontaneous endothermic and increasing the temperature is good for extraction. Therefore, the *isobutyl*-BTP/[C<sub>2</sub>mim][NTf<sub>2</sub>] extraction system is effective to be used at low acidity condition for extraction. These unique properties of the IL based extraction system may help us to design new separation process for hydrometallurgy industry or advanced nuclear fuel cycle application in the future.

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